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(54) Title: A FORMULATION FOR DEPOSITING A LIGHT-EMITTING POLYMER LAYER

(57) Abstract: A formulation for depositing a polymer layer in a light-emitting device, the formulation comprising a conjugated polymer dissolved in a solvent, the solvent comprising at least one substance selected from the group comprising terpenes and polyalkylated aromatic compounds.

A FORMULATION FOR DEPOSITING A LIGHT-EMITTING POLYMER LAYER

The present invention relates to a formulation for depositing a conjugated polymer layer in a light-emitting device (LED).

Light-emitting devices using as the light-emitting layer a semiconductive conjugated polymer are known. Figure 1 shows the construction of a simple light-emitting device. A glass or plastics substrate 2 is coated with an anode layer 4, for example in the form of indium tin oxide. The anode can be patterned in the form of elongate strips. The anode layer may be coated with a hole transport layer. A light-emitting polymer layer 6 is then deposited followed by the deposition of an electron transport layer. The device structure is then completed by the deposition of a cathode layer 8. By way of example, the cathode layer can be calcium or aluminium. The cathode layer 8 can be patterned in crosswise strips to define pixels P where the anode and cathode overlap. Alternatively with an unpatterned cathode, light emitting strips can be defined. Further alternatively, the pixels may be defined on an active matrix back-plane and the cathode may be patterned or unpatterned. When an electric field is applied between the anode and cathode, holes and electrons are injected into the light-emitting polymer layer 6. The holes and electrons recombine in the polymer layer and a proportion decay radiatively to generate light.

The hole transport layer can be comprised generally of any compound capable of sustaining hole transport. Examples of suitable materials are organic conductors such as the following conducting polymers: polyaniline, polyethylenedioxythiophene and other polythiophenes, polypyrrole, etc. in their doped forms. Other alternative

materials are conjugated polyamines and also low molecular weight amines such as TPD.

The light-emissive layer may comprise any molecular or polymeric compounds which are capable of sustaining charge carrier transport and also capable of light emission under device driving conditions. Examples include fluorescent organic compounds and conjugated polymers such as Alq3, polyphenylenes and derivatives, polyfluorenes and derivatives, polythiophenes and derivatives, polyphenylene vinylenes and derivatives, polymers containing hetero-aromatic rings, etc..

The electron transport layer may generally comprise any material capable of sustaining electron transport. Examples include perylene systems, Alq3, polyfluorenes or polyfluorene copolymers, polymers containing heteroaromatic rings, etc..

The device may contain any combination of the above layers provided it includes at least one light-emissive layer.

OLEDs are described in US Patent No. 5,247,190 or in US Patent No. 4,539,507, the contents of which are incorporated herein by reference. In US 5,247,190 the active organic layer is a light-emissive semiconductive conjugated polymer and in US 4,539,507 the active organic layer is a light-emissive sublimed molecular film.

Conventionally, the polymer layer is deposited by spin-coating or metered blade-coating a polymer solution onto the anode and then either allowing the solvent to evaporate at RTP, or driving off the solvent using heat treatment and/or reduced pressure. The polymer can be the light-emitting polymer itself cast directly from solution, or a precursor to the polymer, which is converted to the light-

emitting polymer during a heat treatment step. The polymer layer can comprise a blend of two or more materials, such as a blend of two or more polymers.

The present applicants realised that it is possible to utilise a different deposition technique for depositing the polymer layer in a light-emitting device, as outlined in British Application No. 9808806.5. According to that British application, the light-emitting polymer is deposited by a technique the same as or similar to inkjet printing by supplying a solution-processible material including the polymer through a plurality of elongate bores, either through the effect of gravity or under pressure or utilising the effect of surface tension. This facilitates direct deposition or patterning of the polymer films as required. Figure 2 illustrates the essence of the technique.

It is important to use material formulations with which thin polymer films exhibiting excellent emission uniformity can be produced. In this respect, it is important to use formulations which exhibit the desired properties with respect to surface tension, viscosity, concentration, and contact angle (on the depositing medium and the substrate on to which it is to be deposited), and which preferably also exhibit good solution stability.

It is an aim of the present invention to provide formulations which facilitate the direct deposition of patterned polymer films. In particular, it is an aim of the present invention to provide a formulation with which polymer films which exhibit improved emission uniformity can be deposited, particularly in the context of relatively high molecular weight polymers with intrinsically rigid conjugated systems.

According to one aspect of the present invention there is provided a formulation for depositing a polymer layer in a light-emitting device, the formulation comprising a conjugated polymer dissolved in a solvent, the solvent comprising at least one substance selected from the group consisting of terpenes and polyalkylated aromatic compounds.

According to another aspect of the present invention there is provided a method of depositing a polymer layer by supplying a solution processible formulation via a plurality of elongate bores onto a substrate, wherein the formulation comprises a conjugated polymer dissolved in a solvent, the solvent comprising at least one substance selected from the group consisting of terpenes and polyalkylated aromatic compounds.

The solvent used in the formulation preferably consists substantially of at least one substance selected from the group consisting of terpenes and polyalkylated aromatic compounds. In a preferred embodiment, it consists substantially of a blend of two or more solvents belonging to this group.

The terpene may be a hydrocarbon or comprise one or more functional groups selected from the group consisting of alcohol, ester, ether, ketone and aldehyde groups. Monoterpenes are particularly preferred such as terpinolene, limonene and α -terpineol.

The terpene is in liquid form at the deposition temperature.

Preferred polyalkylated aromatic compounds include polyalkyl benzenes such as cymene and isodurene. It is preferred that each of the alkyl substituents on the

aromatic ring is distinct from each other, i.e. that they are only bonded together via the aromatic ring.

According to one embodiment, the solvent comprises at least one aromatic compound substituted with alkyl groups at no less than 3 positions.

For the purposes of this application, the term conjugated polymer refers to polymers, including oligomers such as dimers, trimers etc., which are fully conjugated (i.e. are conjugated along the entire length of the polymer chain) or are partially conjugated (i.e. which include non-conjugated segments in addition to conjugated segments).

The polymer may be a polymer suitable for use in a light-emissive layer, a hole transport layer or an electron transport layer in an organic light-emitting device.

In a preferred example, the conjugated polymer can be a light-emitting polymer, hole transport polymer or electron transport polymer itself, or a precursor to a light-emitting polymer, hole transport polymer or electron transport polymer. The conjugated polymer or its precursor can be any suitable polymer, and in particular can be any one of the following:

a) conducting polymers such as polyaniline (PANI) and derivatives, polythiophenes and derivatives, polypyrrole and derivatives, polyethylene dioxythiophene; doped forms of all these and particularly polystyrene sulphonic acid-doped polyethylene dioxythiophene (PEDT/PSS);

b) solution processible charge transporting and/or luminescent/electro-luminescent polymers, preferably conjugated polymers such as: polyphenylenes and

derivatives, polyphenylene vinylenes and derivatives, polyfluorenes and derivatives, tri-aryl containing polymers and derivatives, precursor polymers in various forms, copolymers (including the above-named polymer classes), generally random and block copolymers, polymers with the active (charge transporting and/or luminescent) species attached as side-groups to the main chain, thiophenes and derivatives, etc..

It is also envisaged that the present invention is also applicable to formulations comprising other compounds such as solution processible molecular compounds including spiro-compounds, such as described for example in EP-A-0676461; and other inorganic compounds, e.g. solution-processible organometallic precursor compounds to fabricate insulators or conductors.

The specific example discussed herein is a blend of 5BTF8 (80% in weight) and TFB (20%).

For a better understanding of the invention and to show how the same may be carried into effect, reference will now be made by way of example to the accompanying drawings in which:

Figure 1 is a diagram of a light-emitting device;

Figure 2 is a diagram illustrating a method of depositing various polymer layers;

Figures 3a to 3e represent the structures of isodurene, terpinolene, limonene cymene and α -terpineol respectively;

Figures 4a to 4c illustrate the formulae of TFB and 5BTF8;

Figure 5 is a graph of optical density versus time illustrating the improved solubility stability of the solvents discussed herein;

Figure 6 is a graph showing the photoluminescent properties of a polymer layer deposited in isodurene; and

Figure 7 is a graph comparing the photoluminescent properties of a polymer deposited in isodurene-terpinolene (3:1) and xylene.

Figure 2 illustrates a deposition technique for depositing a polymer layer 6 onto the patterned anode 4. A plurality of elongate bores 10 are illustrated, each aligned with a respective trough 8. The elongate bores 10 are connected via a conduit 12 to a reservoir 14 holding the solution to be deposited. The solution is supplied through the elongate bores 10 under pressure or by gravity to deposit the light emitting polymer layer 6. Specific formulations for the solution processible material 16 are discussed herein.

Example 1

The first exemplified formulation is 0.5% W/V of 5BTF8 (80% in weight) and TFB (20%) in isodurene. The structure of TFB is illustrated in Figure 4a. 5BTF8 is F8 (structure of Figure 4b) doped with 5% F8BT (structure of Figure 4c).

Example 2

According to the second example, the formulation comprises 0.5% W/V of 5BTF8 (80% in weight) and TFB (20%) in a solvent comprising a blend of isodurene:terpinolene (3:1).

Example 3

According to a third example, the formulation comprises 0.5% W/V of 5BTF8 (80% in weight) and TFB (20%) in isodurene:limonene (3:1).

Example 4

According to a fourth example, the formulation comprises 0.5% W/V of 5BTF8 (80% in weight) and TFB (20%) in isodurene:cymene (3:1).

Using the formulation according to each example, a polymer layer was deposited using the technique described in relation to Figure 2. The solubilities were measured with over a 48 hour period at 17°C. The results are plotted in Figure 5, from which it can readily be seen that they display excellent stability of solubility over that period.

Subsequently, the photoluminescent properties of Examples 1 and 2 were compared with photoluminescent properties of a polymer deposited using a xylene solvent. Figure 6 illustrates the results of Example 1, where the solvent is isodurene and Figure 7 illustrates the results for Example 2 where the solvent is isodurene-terpinolene (3:1). Figure 6 and 7 also illustrate the case where the polymer layer deposited in the novel solvent is heat-treated after deposition.

As can be seen, there are no significant changes in the photoluminescent properties as regards the wavelength of emission. Thus, a light-emitting device can be manufactured with known and specified light-emission properties, but with significant improvements in stability by using the novel formulations defined herein.

CLAIMS:

1. A formulation for depositing a polymer layer in a light-emitting device, the formulation comprising a conjugated polymer dissolved in a solvent, the solvent comprising at least one substance selected from the group comprising terpenes and polyalkylated aromatic compounds.
2. A formulation according to claim 1 wherein the terpene is a monoterpene.
3. A formulation according to claim 1 or claim 2, wherein the terpene is a hydrocarbon or comprises one or more groups selected from alcohol, ester, ether, ketone and aldehyde groups.
4. A formulation according to claim 2 or claim 3 wherein the terpene is one selected from the group consisting of terpinolene, limonene and α -terpineol.
5. A formulation according to claim 1 wherein the polyalkylated aromatic compound is a polyalkylated benzene.
6. A formulation according to claim 5 wherein the polyalkylated benzene is a dialkylbenzene.
7. A formulation according to claim 6 wherein the dialkylbenzene is selected from the group consisting of cymene, diethylbenzene, 1-methyl-4-t-butylbenzene.
8. A formulation according to claim 5 wherein the polyalkylated benzene is a tetraalkylbenzene.
9. A formulation according to claim 8 wherein the tetraalkylbenzene is isodurene.

10. A formulation according to any preceding claim, wherein the polymer is a light-emissive polymer.
11. A formulation according to claim 1 wherein the polymer comprises a fluorene-based polymer.
12. A formulation according to claim 1 wherein the polymer comprises a polymer containing fluorene and triarylamine units.
13. A formulation according to claim 1 wherein the polymer comprises a blend of a fluorene-based polymer and a polymer containing fluorene and triarylamine units.
14. A formulation according to claim 13 wherein the polymer is a blend of 5BTF8 and TFB.
15. A formulation according to claim 14, wherein the constituents of the polymer blend are 5BTF8 (80%); TFB (20%).
16. A formulation according to any preceding claim, wherein the solvent comprises a blend of two or more of said substances.
17. A formulation according to claim 16 wherein the blend comprises two or more substances selected from the solvent group consisting of isodurene, cymene, terpinolene, limonene and α -terpineol.
18. A formulation according to claim 17, wherein the blend contains 3 parts isodurene to 1 part of another member of the solvent group.
19. A formulation according to claim 18, wherein the blend is isodurene:terpinolene (3:1).

20. A formulation according to claim 18, wherein the blend is isodurene:limonene (3:1).

21. A formulation according to claim 18, wherein the blend is isodurene:cymene (3:1).

22. A method of depositing a polymer layer by supplying a solution processible formulation via a plurality of elongate bores onto a substrate, wherein the formulation comprises a conjugated polymer dissolved in a solvent, the solvent comprising at least one substance selected from the group consisting of terpenes and polyalkylated aromatic compounds.

1 / 3

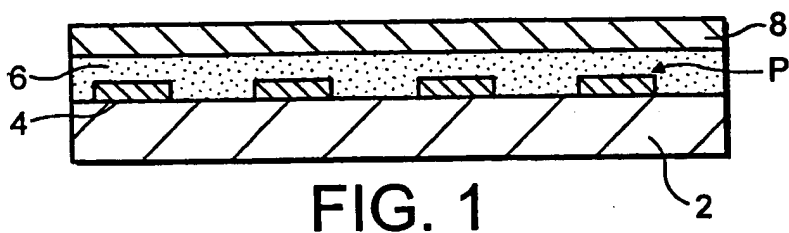


FIG. 1

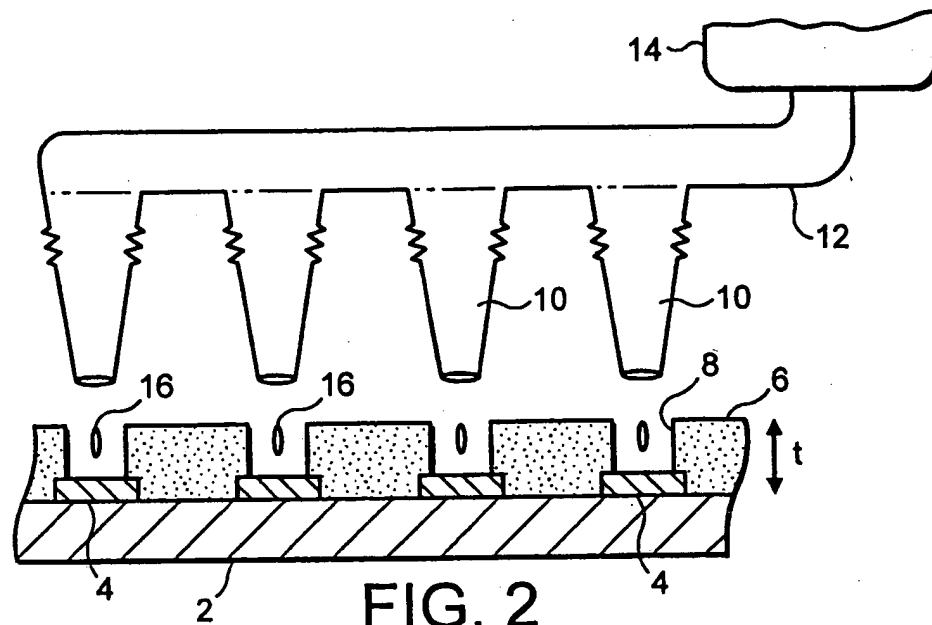
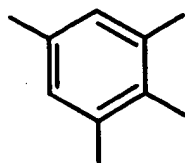
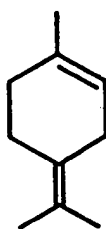


FIG. 2



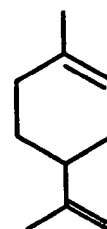
ISODURENE

FIG. 3a



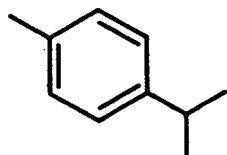
TERPINOLENE

FIG. 3b



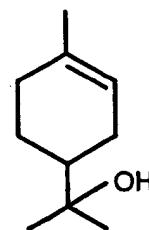
LIMONENE

FIG. 3c



CYMENE

FIG. 3d



α -TERPINEOL

FIG. 3e

2 / 3

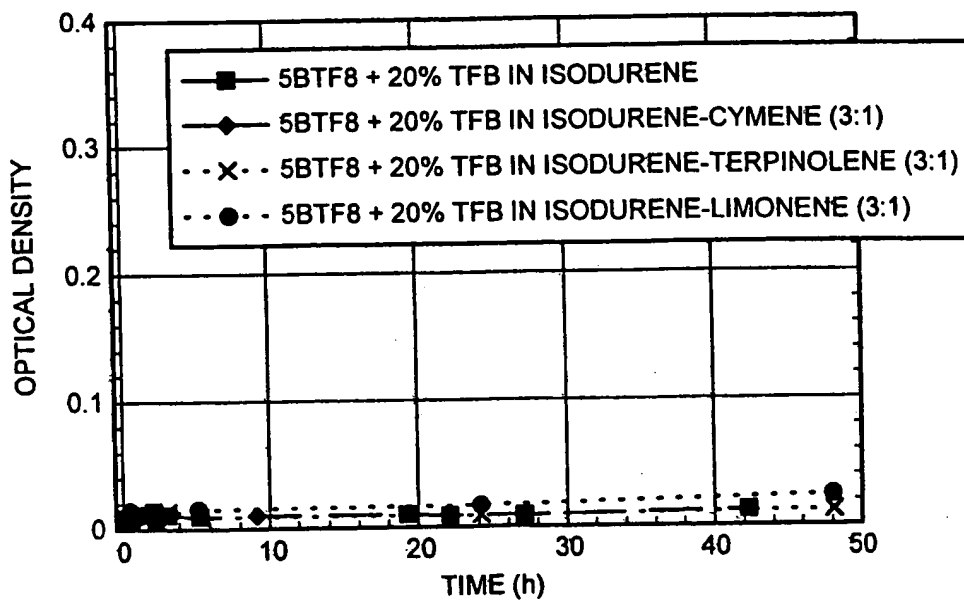
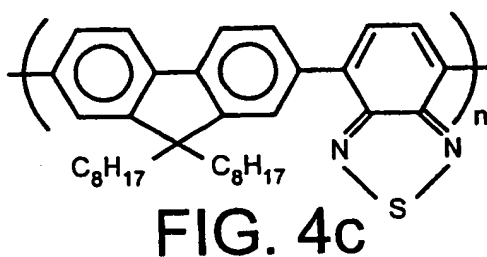
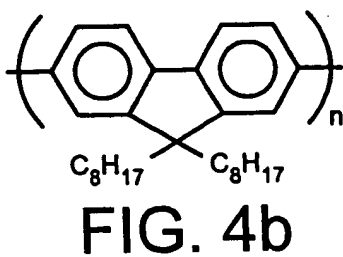
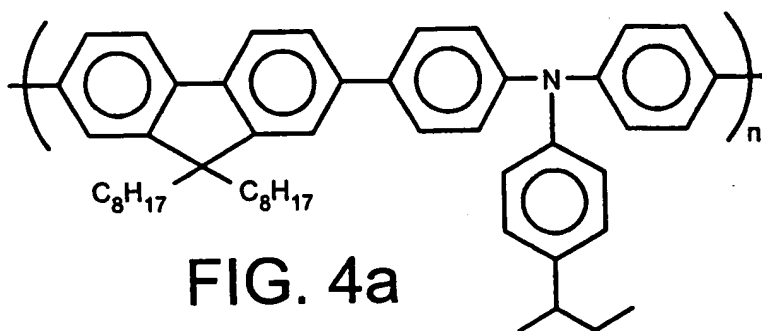


FIG. 5

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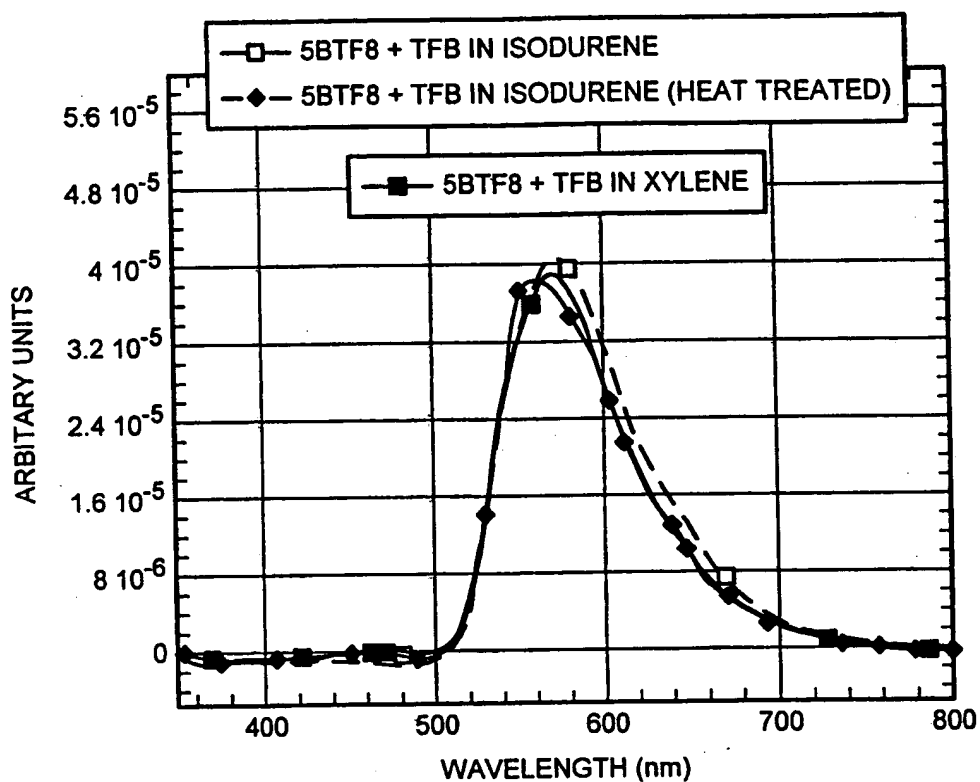


FIG. 6

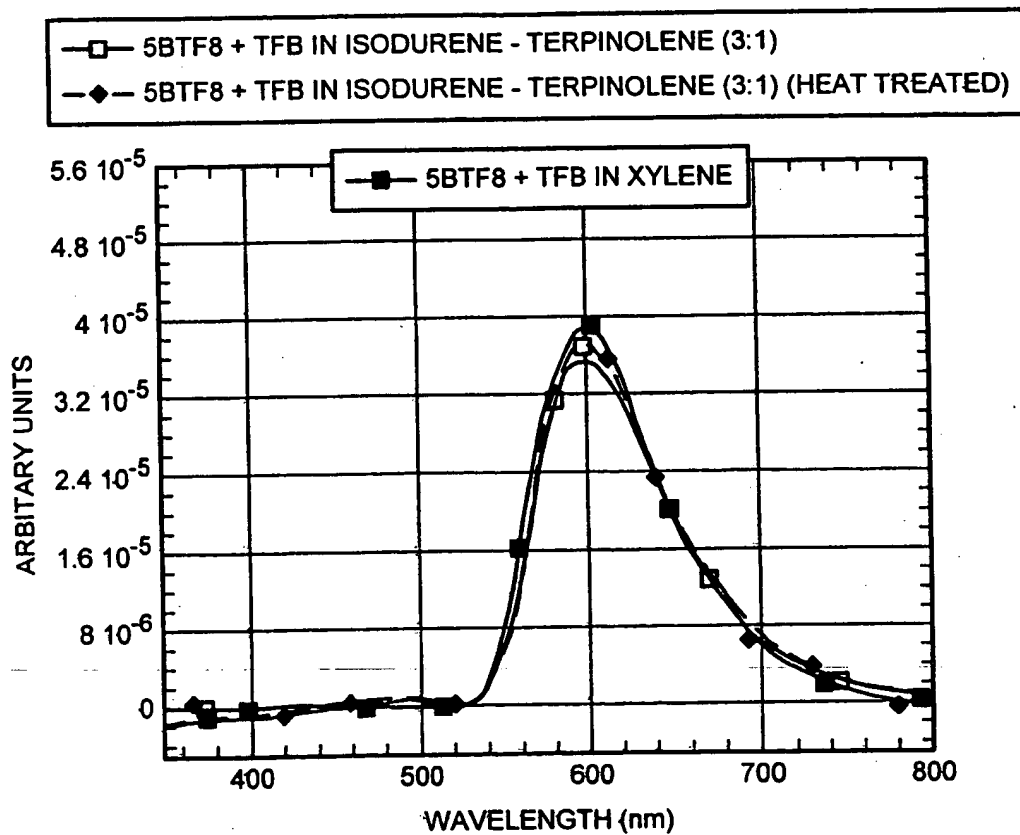


FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/03349

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K11/06 H05B33/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K C08G H01L H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 13692 A (BURROUGHES JEREMY ; GREENHAM NEIL CLEMENT (GB); BRIGHT CHRIS (GB);) 18 March 1999 (1999-03-18) page 29, paragraph 2	1,5,6, 10,11
P, X	WO 99 54385 A (DOW CHEMICAL CO) 28 October 1999 (1999-10-28) example 1B	1,5,6, 10,11, 13,14
X	EP 0 923 083 A (KEMET ELECTRONICS CORP) 16 June 1999 (1999-06-16) column 2, line 7 - line 9; claims 1,11; example 1	1-6,16, 17
X	US 5 912 473 A (HOTTA SHU ET AL) 15 June 1999 (1999-06-15) example 8	1,5,6,10

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/03349

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 777 070 A (INBASEKARAN MICHAEL ET AL) 7 July 1998 (1998-07-07) column 7, line 49 - line 50; examples 1,5 ---	1,5,6, 10-15
X	EP 0 825 242 A (SUMITOMO CHEMICAL CO) 25 February 1998 (1998-02-25) page 9, line 22 - line 25 ---	1,5,6
A	WO 99 12398 A (CAMBRIDGE DISPLAY TECH ;FRIEND RICHARD HENRY (GB)) 11 March 1999 (1999-03-11) page 14, paragraph 4 -page 15, paragraph 1 ---	10-15
P,A	GB 2 336 553 A (CAMBRIDGE DISPLAY TECH) 27 October 1999 (1999-10-27) cited in the application figure 1 ---	22
A	EP 0 609 478 A (SPECIALTY COATING SYSTEMS INC) 10 August 1994 (1994-08-10) claim 1 -----	22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/03349

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9913692 A	18-03-1999	AU 8991598 A EP 1010360 A WO 9948337 A	29-03-1999 21-06-2000 23-09-1999
WO 9954385 A	28-10-1999	CN 1263542 T EP 0988337 A	16-08-2000 29-03-2000
EP 0923083 A	16-06-1999	US 5888582 A CZ 9804036 A JP 11246822 A US 5948234 A	30-03-1999 15-09-1999 14-09-1999 07-09-1999
US 5912473 A	15-06-1999	US 5546889 A US 5556706 A JP 7206599 A	20-08-1996 17-09-1996 08-08-1995
US 5777070 A	07-07-1998	EP 1025142 A WO 9920675 A	09-08-2000 29-04-1999
EP 0825242 A	25-02-1998	JP 10114891 A	06-05-1998
WO 9912398 A	11-03-1999	NONE	
GB 2336553 A	27-10-1999	DE 19918193 A JP 2000202357 A	25-11-1999 25-07-2000
EP 0609478 A	10-08-1994	CA 2088851 A FI 930518 A JP 6233962 A NO 930407 A US 5266349 A	06-08-1994 06-08-1994 23-08-1994 08-08-1994 30-11-1993